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Optimization of the spin entropy by incorporating magnetic ion in a misfit-layered calcium cobaltite

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ABSTRACT

Effects of (Lu, Ni) co-doping on spin entropy of $Ca_3Co_4O_{9+\delta}$ have been investigated. Results of this study show that (Lu, Ni) co-doping can be more effective than single Lu doping for optimizing the spin entropy of $Ca_3Co_4O_{9+\delta}$. X-ray photo-emission spectroscopy confirms a reduction in Co^{4+} concentration, which leads to enhanced spin entropy from Co sites. The magnetic ions of Ni with unpaired 3d electrons can produce extra spin entropy through a new hopping model, thereby contributing to an increase in total spin entropy. Incorporating magnetic ions is an effective way to optimize the spin entropy of thermoelectric materials. This study opens a new way to broaden and design prospective thermoelectric materials.

1. Introduction

Thermoelectric materials, which involve conversion between thermal and electrical energy, help alleviate global problems in energy supply [1–3]. The efficiency of thermoelectric materials can be coupled directly to the dimensionless figure of merit using the following equation: $ZT=S^2\sigma T/\kappa$. This equation indicates that advanced thermoelectric materials require high thermopower S, high electrical conductivity σ, and low thermal conductivity κ. $Ca_3Co_4O_{9+\delta}$ (CCO) has long been considered as a perfect misfit-layered cobalt oxide and a reliable contender for p-type thermoelectric materials because of its thermal and chemical stability at high temperature and good thermoelectric performance [4–8]. The CCO consists of two alternating subsystems. Each subsystem satisfies a varied role in obtaining high thermoelectric properties. Along with the c-axis of CCO, CdI_2-type CoO_2 layers are detached by a triple coating of an insulating rock-salt type shape. CoO_2 acts as a good conductive p-type electron crystal, and the insulating Ca_2CoO_3 behaves as a charged reservoir and phonon-glass layer [7,8].

Substantial experiments [10–12] and theoretical efforts have been directed to reveal the source of large thermopower in misfit-layered cobalt oxides. The large thermopower has been qualified to a few different mechanisms [4,9]. Many theoretical studies suggest that spin entropy plays a significant role in improving the thermopower in cobalt oxides [13,14]. Several experimental studies support spin entropy theory [15–18]. Wang et al. [15] found the suppression of the thermopower in $NaCo_2O_4$ under a longitudinal magnetic field at low temperatures and suggested the spin entropy as a major source of the observed large thermopower. Limelette et al. [19] observed a scaling behavior with both temperature and magnetic field in a misfit cobalt oxide, which reveals a strong spin entropy contribution to thermopower. Zhang et al. [20] recently reported scaling behavior of the thermopower in LaBaCoO, which indicates that the spin entropy is the origin of the thermopower of cobalt oxides. This study previously observed strong field dependencies for both out-of-plane and in-plane thermopower in CCO single crystal and disclosed that the spin entropy dominates the thermopower in CCO [21,22]. Spin entropy can be enhanced by suppressing Co^{4+} concentration in CCO [21–25]. One of the most prominent properties of magnetic ions is that the degeneracy of the electronic configuration in real space can result in extra entropy, which contributes to the rise of the spin entropy in layered cobalt oxides [18,26]. This condition motivates the exploration of outstanding thermoelectric materials with magnetic ions. Combining the magnetic transition metal, Ni, can be an excellent approach to the possible optimization of the spin entropy and thermopower. Therefore, this study investigates whether Lu and the magnetic transition metal Ni co-doping could significantly increase the spin entropy of CCO.

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The effects of (Lu, Ni) co-doping on the spin entropy of CCO have been examined. The results reveal that (Lu, Ni) co-doping is more effective than the single Lu doping in increasing and improving the spin entropy, which confirms the incorporation of magnetic ions as an effective approach to optimize the spin entropy of thermoelectric materials. This study adopts a suitable mechanism to explain experimental observations.

2. Experimental

This study prepared polycrystalline samples of $Ca_{3-x}Lu_xCo_{4-y}Ni_yO_{9+\delta}$ in a sol–gel chemical solution route. Stoichiometric $CaCO_3$, $Co(NO_3)_2\cdot 6H_2O$, $Lu(NO_3)_3\cdot 6H_2O$, $Ni(NO_3)_2\cdot 6H_2O$, and citric acid monohydrate were dissolved in distilled water. The mixed solution was dehydrated at 335 K for 12 h. The resulting gel was heated at 473 K for 3 h to remove moisture. After cooling to room temperature, the obtained powders were ground and sintered at 1173 K for 12 h and pressed into pellets. Finally, the black pellets were annealed at 1173 K for 36 h under O_2 atmosphere.

X-ray diffraction (XRD) analysis was implemented on a Rigaku diffractometer with Cu Kα radiation. The range of 2 theta in XRD analysis was 10–70°, and the wave length of Cu Kα 1 and Cu Kα 2 were 0.15406 nm and 0.15443 nm, respectively. The thermopower measurements from 20 K to 300 K were fulfilled by utilizing a commercial quantum design physical property measurement system. The direction of the magnetic field (4 T) for magnetothermopower measurements was parallel to the temperature gradient. X-ray photoemission spectroscopy (XPS) experiments were conducted on a PHI 500 VersaProbe spectrometer equipped with monochromatized Al Kα radiation. The energy of XPS survey spectra was measured from 1 eV to 1000 eV, and valence-band XPS spectra was conducted from 0 eV to 1 eV. The high-resolution XPS spectra of Co, Lu, and Ni elements were fitted and analyzed systemically.

3. Results and discussion

The XRD patterns of $Ca_{3-x}Lu_xCo_{4-y}Ni_yO_{9+\delta}$ are shown in Fig. 1. All of the diffraction peaks are consistent with the standard JCDPDS card (No. 21-0139) of CCO phase with monoclinic

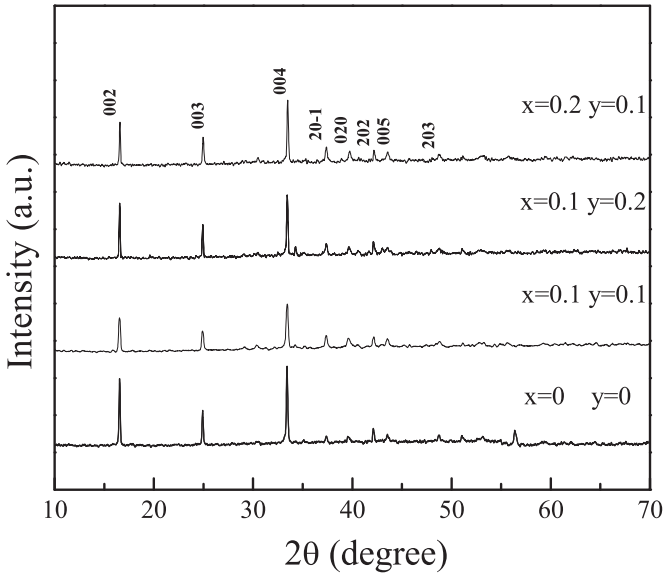

Fig. 1. XRD patterns of $Ca_{3-x}Lu_xCo_{4-y}Ni_yO_{9+\delta}$ samples.

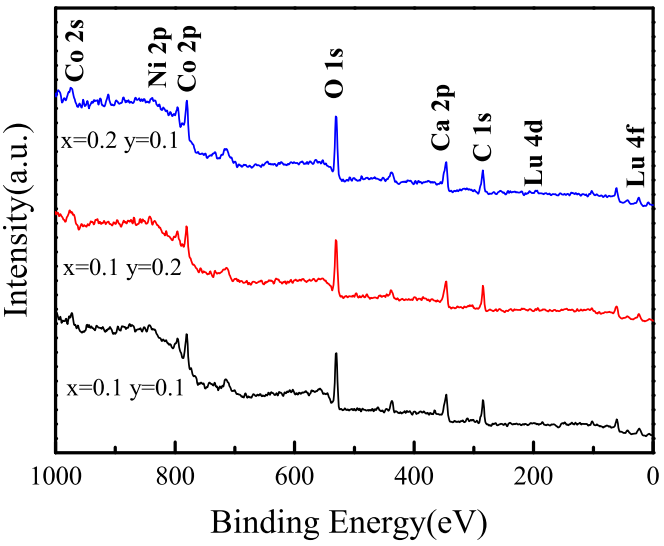

Fig. 2. XPS survey spectra of $Ca_{3-x}Lu_xCo_{4-y}Ni_yO_{9+\delta}$ samples.

symmetry, which indicates that single-phase compounds are obtained [5]. The main constituents of elements is demonstrated by the XPS survey spectra of $Ca_{3-x}Lu_xCo_{4-y}Ni_yO_{9+\delta}$ (Fig. 2), which indicate that Lu and Ni have been doped into the lattices of CCO.

Fig. 3 presents the thermopower (S) as a function of temperature ranges from 20 K to 300 K for $Ca_{3-x}Lu_xCo_{4-y}Ni_yO_{9+\delta}$ series. The S of all samples rises monotonically with increasing temperature. The positive S values of all samples indicate that holes are the major carriers of the (Lu, Ni) co-doped specimens. All co-doped samples exhibit significantly enhanced S compared with the pristine CCO. The maximum S for the $Ca_{2.9}Lu_{0.1}Co_{3.9}Ni_{0.1}O_{9+\delta}$ sample reaches 110 μV/K at 300 K.

A series of magnetothermopower measurements is conducted for $Ca_{3-x}Lu_xCo_{4-y}Ni_yO_{9+\delta}$ samples at an applied magnetic field of 4 T to investigate the effects of (Lu, Ni) co-doping on the spin entropy. A clear field-induced decrease is observed in S (Fig. 4). Partial spin degeneracy is removed by an applied magnetic field. Thus, a representative signature of a spin entropy declines and reveals a large spin entropy contribution to S in these materials [15–17]. The spin entropy reduces as spins are forced to align with the magnetic field. The temperature dependence of

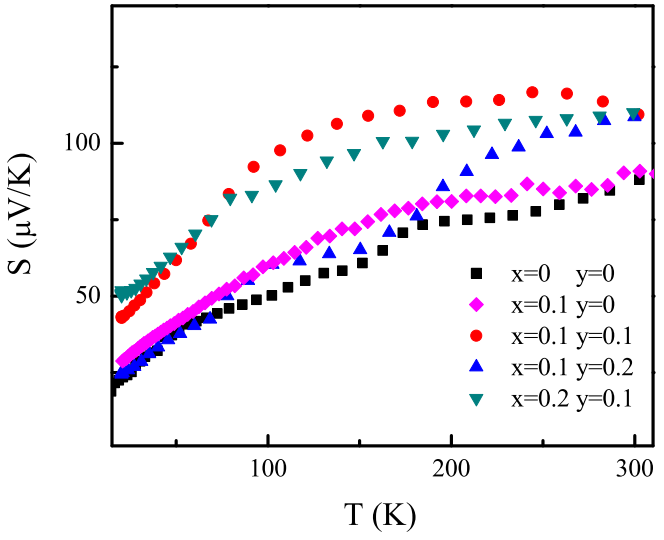

Fig. 3. Temperature dependence of thermopower for $Ca_{3-x}Lu_xCo_{4-y}Ni_yO_{9+\delta}$ samples.